

## Commercialization Analysis & Roadmap

Title: Polyaniline-Based Membranes for Separating CO<sub>2</sub> & CH<sub>4</sub>

Date: February 5th, 2013

IB# 3129

Researchers (PI\*): Frantisek Svec\*, Natalia Blinova

### Technology

Berkeley Lab researchers have optimized polymer membrane technology to more efficiently remove carbon dioxide (CO<sub>2</sub>) from natural gas. The invention employs an in-situ deposition technique that enables the fabrication of a multilayered composite membrane. In particular, the membrane combines readily available porous polypropylene as a supporting film with an ultrathin (150 nanometers or less), homogeneous, defect-free polyaniline (PANI) layer [1,2]. Modifications activating the surface for reaction with diamines and enabling accommodation of a polyethylene glycol layer make the surface more hydrophilic and facilitate CO<sub>2</sub> transport. The result is a membrane with unprecedented permeability and selectivity.

This technology's separation performance negates the need for a multiple stage membrane. After solvation with water, these membranes exhibit a high permeability of around 3,460 Barrers and a remarkable separation factor of up to 540 [3]. In comparison, current industrial membranes (such as cellulose acetate and polyimide technologies) exhibit modest selectivity of 12-15 and 20-25 respectively, and thus do not compete with the separation performance of the LBNL's PANI membrane []. Below is a Robeson's plot of the empirical permeability/separation factor and upper bound relationship for separation of CO<sub>2</sub>/CH<sub>4</sub> using membranes. The colored experimental data points on the top right show the permeability and separation factor  $\alpha$  determined for the Berkeley Lab surface-modified PANI membrane in three different tests. The exceptional performance of the membrane significantly exceeds all other results included in the plot.

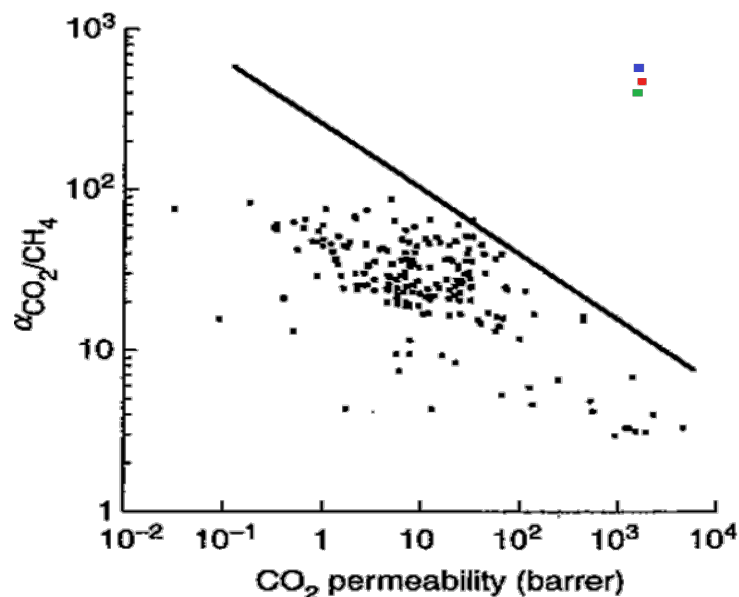
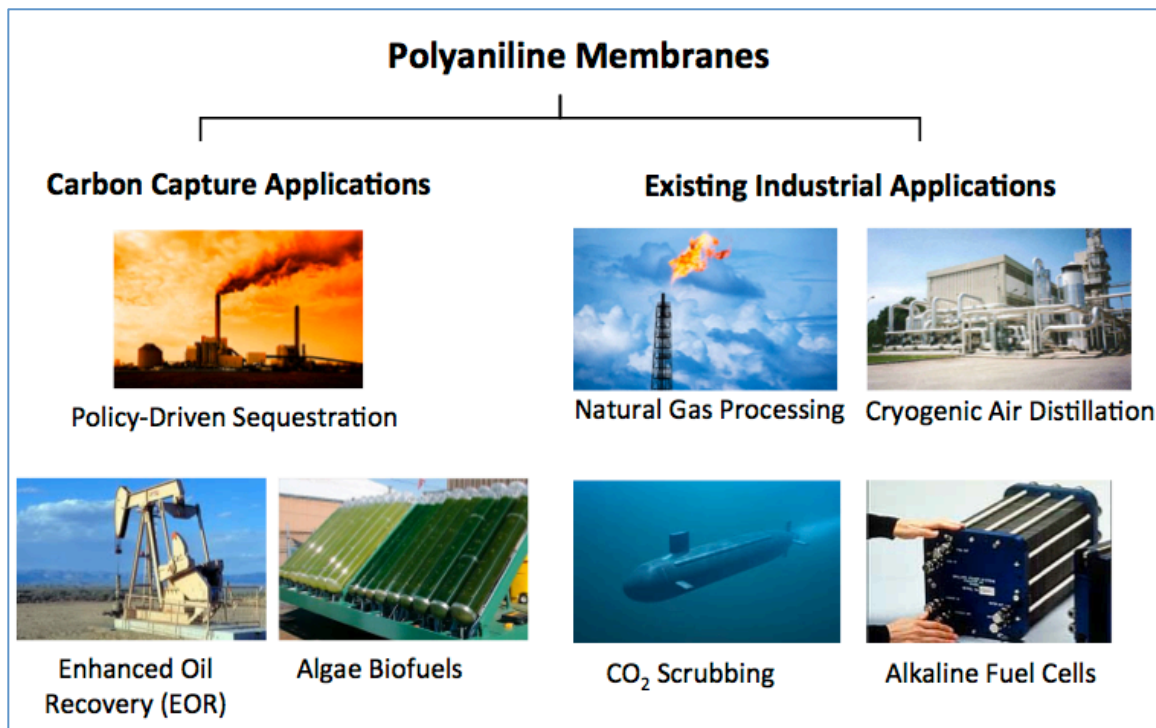


Figure 1 - Robeson's plot of the empirical permeability/separation factor and upper bound relationship for separation of CO<sub>2</sub>/CH<sub>4</sub> using membranes [3].

## Applications



### Separation of carbon dioxide from natural gas in:

- Oil refineries
- Petrochemical plants
- Natural gas processing plants
- Agricultural methane processing plants
- Landfill gas utilization

This separation process is also referred to as 'sweetening' of natural gas, whereby sour gas containing acidic gases such as foul-smelling hydrogen sulfite, and carbon dioxide (which decreases the energy content of the gas and increases transportation costs) are removed. These harmful gases form acids upon contact with water, which are highly corrosive to pipelines.

Ideally, this separation technology would be applied at the natural gas source (i.e. the well) to avoid transportation costs of the CO<sub>2</sub> and improve efficiency in later stage combustion processing.

### Separation of carbon dioxide from flue gas (mainly N<sub>2</sub>) in:

- Oil refineries
- Petrochemical plants
- Chemical plants
- Power plants
- Incinerators

### Separation of carbon dioxide from Hydrogen gas in:

- Hydrogen plants
- Coal gasification electric power plants
- Oil refineries
- Petrochemical plants

#### CO<sub>2</sub> scrubbing

The polyaniline membranes can be used in spacecraft, submarines, and re-breather scuba gear to maintain a CO<sub>2</sub> free environment. In addition, re-breather technology is used in mine rescue, mountaineering, firefighting, and hospital anesthesia breathing systems.

#### Alkaline fuel cells

The polyaniline membranes can prevent CO<sub>2</sub> contamination in alkaline fuel cells – some of the most efficient fuel cells today. In particular, CO<sub>2</sub> in the cathode's air stream poisons the electrolyte, and in some cases clogs the electrode as a result of carbonate build up. Used by NASA in Apollo-series missions and on the Space shuttle, this relatively cheap fuel cell is a good candidate for further efficiency improvement.

### **Market**

Amine-based absorption with an aqueous monoethanolamine (MEA) solution is one of the most commonly used technologies for post-combustion capture, since it is capable of achieving a high level of CO<sub>2</sub> capture (90% or more) from flue gas due to fast kinetics and strong chemical reaction. However, the amines are corrosive and susceptible to degradation by trace flue gas constituents (particularly sulphur oxides) and require a significant amount of energy (in the range 4–6 MJ/kgCO<sub>2</sub> recovered) principally for regeneration. This option requires large-scale equipment for the CO<sub>2</sub> removal and chemicals handling. Likewise, physical solvent technologies such as Selexol<sup>TM</sup> and Rectisol<sup>®</sup> are also being used widely in commercial applications as the go-to technologies for pre-combustion carbon capture. However as innovation advances and the cost reduction benefit of CCS increases, the DOE forecasts that the next technology to supersede MEA and physical solvents will be membrane systems. The commercialization timeline below (Figure 2) shows the landscape of CCS technologies [5].

In 2010, the United States alone used 24.64 trillion cubic feet of natural gas (= 7.5 trillion m<sup>3</sup>). Such consumption of natural gas drives a worldwide market for new natural gas separation equipment of ~5 billion per year [6]. In 2007, membrane processes had <5% of this market, almost all of which is applied toward the removal of carbon dioxide [6]. The current \$3.7 billion US membrane industry is expected to increase 7.7% per year to \$5.4 billion in 2016 as membrane technology continues to compete against typical absorption processes [7].

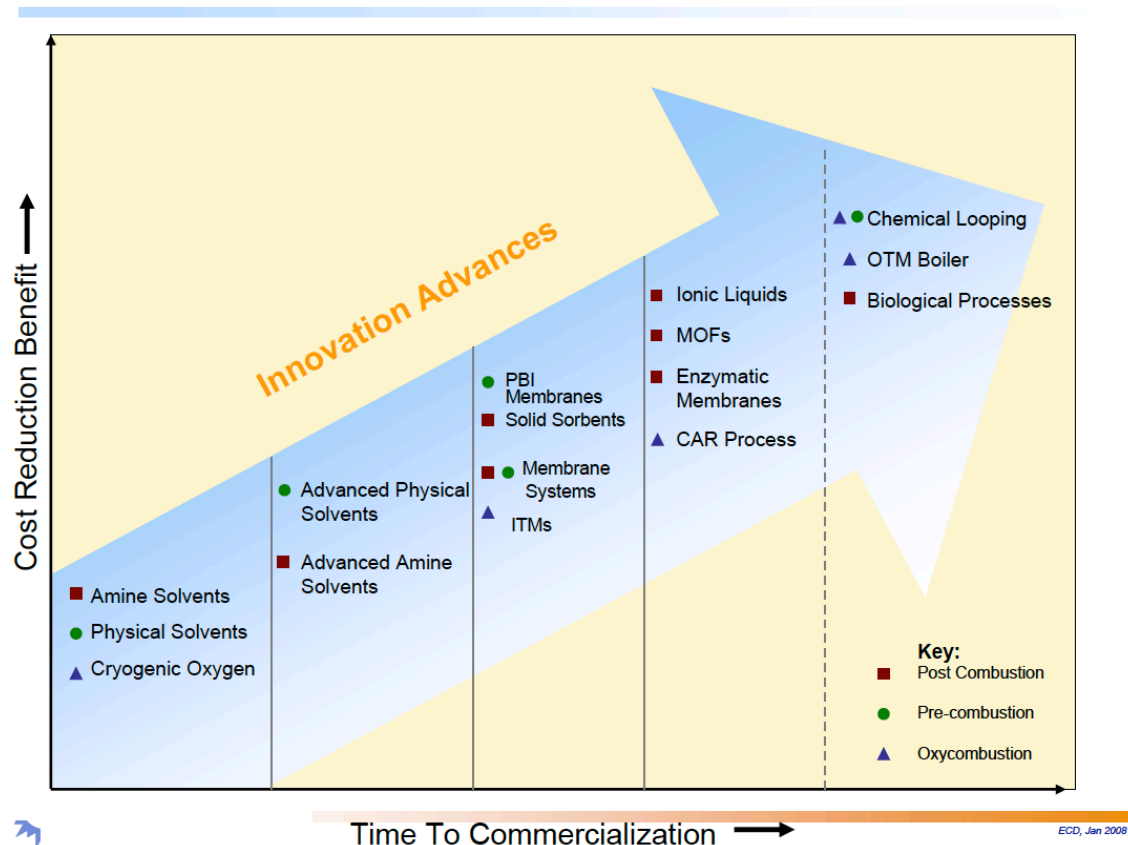


Figure 2 - The landscape of CCS technologies as applied to the oil and gas industry [5]

Much of the focus of debate on developing carbon capture technology has been on research, development, and demonstration (RD&D) needs. However, for technology to be fully commercialized, it must meet a market demand—a demand created either through a price mechanism or a regulatory requirement [4]. Carbon-capture technology for coal-fired power plants directly translates to an increase in the cost of electricity generation from affected plants with no increase in efficiency. Hence, widespread adoption of CCS technology will be challenging until it is driven either by regulation or by a carbon price. Currently, firms have no incentive to reduce their greenhouse gas emissions beyond the motivation to economize on energy costs [4]. Table 1 below shows the regulatory policies of major CO<sub>2</sub> emitting nations. Nonetheless, niche markets that monetize CO<sub>2</sub> scrubbing technologies present a formidable alternative to this membrane technology.

Table 1 – Regulatory policies of Major CO<sub>2</sub> Emitters circa 2008 [8]

Region	Overview	Policy Type	CO <sub>2</sub> \$/ton
United States	Regional initiatives	Cap-and-trade	3-5
Europe	Multi-national policy	Cap-and-trade	15-44
China	National plan	N/A	N/A
Australia	National policy	Tax → Cap/trade	13-27
New Zealand	National policy	Cap-and-trade	10-20

Source: CO<sub>2</sub> Emissions Database, IEA Greenhouse Gas R&D Programme.

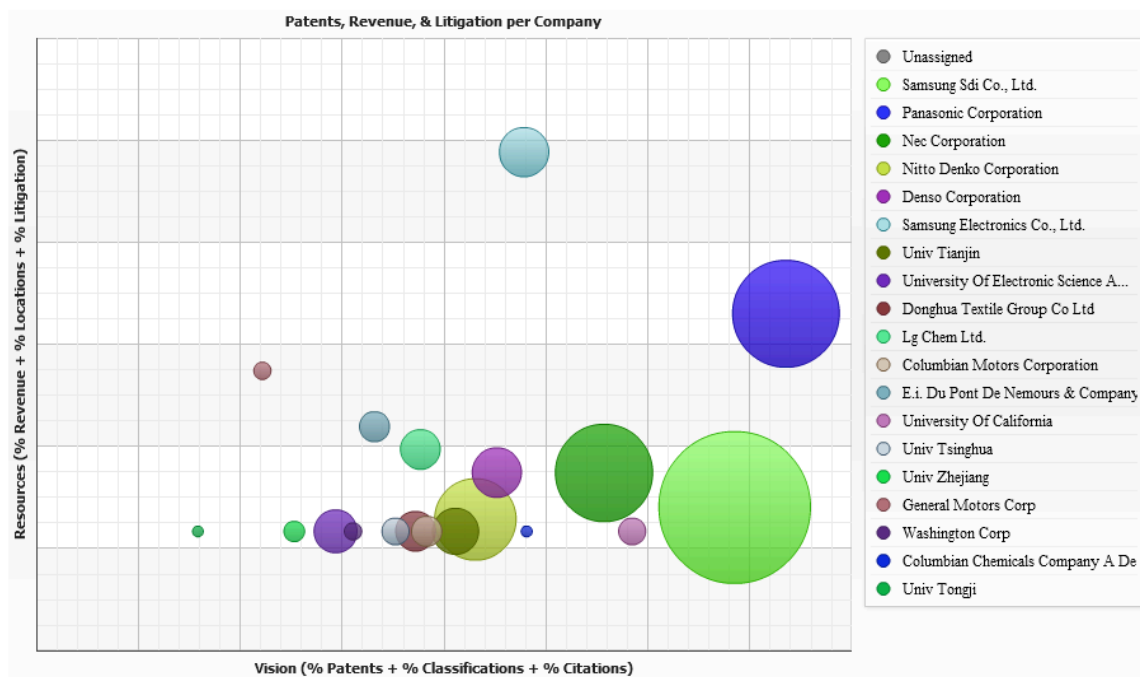
## Economics

**Table 2 - Range of CO<sub>2</sub> Capture Costs for several Types of Industrial Processes [9]**

(2007\$/tonne CO<sub>2</sub>)

Industrial Process	Capture Cost Range
Fossil fuel power plants	\$20-\$95/t CO <sub>2</sub> net captured
Hydrogen and ammonia production, or a natural gas processing plant	\$5-\$70/t CO <sub>2</sub> net captured
All other industrial processes	\$30-\$145/t CO <sub>2</sub> net captured

## Competitive Landscape



**Figure 3 - Chart demonstrating that global innovation is active in driving membrane solutions for CO<sub>2</sub> capture**

## Driving Forces

The United States Department of Energy (DOE) has set two cost goals in its Carbon Sequestration Program: (1) CO<sub>2</sub> capture technologies for a greenfield PC plant should achieve 90 percent CO<sub>2</sub> capture with an increase in the cost of electricity (COE) of no more than 20 percent, and (2) CO<sub>2</sub> capture technologies for coal gasification should achieve 90 percent capture with no more than a 10 percent increase in COE. Current technology cannot achieve these targets. The regulation of the carbon dioxide emissions implies the development of specific CO<sub>2</sub> capture technologies that can be retrofitted to existing power plants as well designed into new plants with the goal to achieve 90% of CO<sub>2</sub> capture limiting the increase in cost of electricity to no more than 35% [10].

The Department of Energy's National Energy Technology Laboratory (DOE/NETL) has estimated that MEA-based process for CO<sub>2</sub> capture will increase the cost of the electricity for a new power plant by

about 80–85%, also reducing the plant efficiency of about 30%. However initial studies show that the cost of electricity increase using membrane technology can be reduced to 14%, as shown in the table below [11].

**Table 3 - Preliminary Economic Analysis showing membrane technology improvement in energy capture efficiency; Polymer technology (PBI) approaches the DOE goals of CCS [11]**

*CO<sub>2</sub> capture: 3.3 Million tonnes/yr.*

	Units	Project Cases			
		No Capture	CO <sub>2</sub> and H <sub>2</sub> S Capture w/Selexol	CO <sub>2</sub> Capture w/PBI & H <sub>2</sub> S w/Selexol	CO <sub>2</sub> Capture w/PBI no H <sub>2</sub> S removal
Power Production @100% Capacity	GWh/yr	5,455	4,461	4,943	5,035
Power Plant Capacity	cents / kWh	4.50	6.19	5.49	5.02
Power Plant Fuel	cents / kWh	1.90	2.47	2.31	2.26
Variable Plant O&M	cents / kWh	0.78	1.00	0.92	0.91
Fixed Plant O&M	cents / kWh	0.60	0.79	0.71	0.70
Power Plant Total	cents / kWh	7.78	10.45	9.43	8.89
Cost of Electricity* (COE)	cents / kWh	7.78	10.45	9.43	8.89
Increase in COE (over no capture)	%	n/a	34%	21%	14%

\* Separation and Capture Only

*Plant operating life: 30 years; Capacity Factor: 80%; Capital charge factor: 17.5%*

*Capture with Selexol uses slightly different parameters than NETL cases.*

With regard to momentum in the re-breather niche market, in August 2012 the U.S. National Institute of Occupational Safety and Health (NIOSH) commissioned a project to improve the systems used by miners in emergency systems. The Underwater Systems Development and Acquisition Branch of the Naval Surface Warfare Center, Panama City division received the funding to research re-breather technology geared towards mining. The team is currently looking to enhance the re-breather – either by applying their expertise to modify the current diving rigs or producing an entirely new product [12]. As such, this is a potential avenue for collaboration with LBNL's polyaniline membrane CO<sub>2</sub> capture technology.

## Advantages

PANI has excellent stability, readily available monomers, simple scalable preparation, potential ability to form homogeneous thin layers, and compatibility with other polymers. This membrane technology optimizes the compromise between permeability and selectivity and does not require multiple stages to sufficiently meet CO<sub>2</sub> capture performance targets. In addition, the in situ deposition technique enables the formation of defect-free composite membranes combining polyaniline as an active layer with a porous polypropylene support.

## Challenges

Because of their modular nature and the need for relatively large surface areas, membrane systems do not have the economies of scale with plant size found in other types of capture systems. Nonetheless, scale up is possible through high density hollow fiber membrane formations that provide larger mass transfer interfaces thereby increasing both capacity and efficiency.

Other common issues with using membranes for CO<sub>2</sub> removal include temperature and chemical resistance. The high temperatures of flue gases may destroy the membrane, so the gases need to be cooled to below 100°C, prior to membrane separation. Likewise, the membranes will need to be chemically resistant to the harsh chemicals contained within flue gases, or these chemicals will need to be removed prior to the membrane separation step.

### Intellectual Property

Patent application pending. The technology is available for licensing or collaborative research. Contact [ttd@lbl.gov](mailto:ttd@lbl.gov)

### Readiness

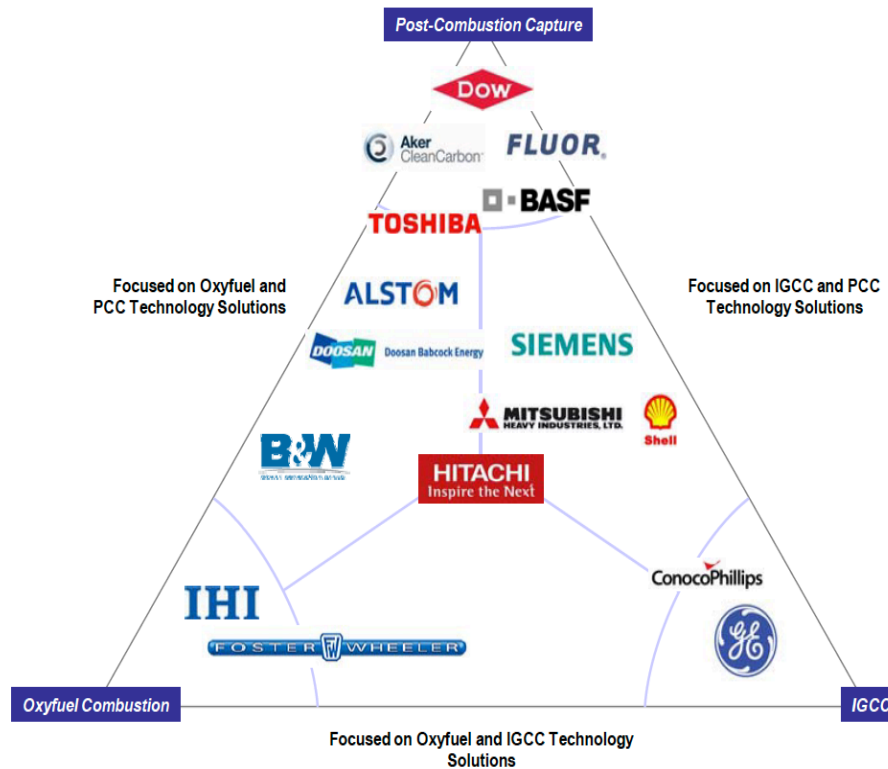
**Table 4 – Various Planned Demonstration Projects with Full-scale Pre-Combustion Capture [9]**

Project Name and Location	Plant and Fuel Type	Expected Year of Startup	Plant Size or Capacity	CO <sub>2</sub> Capture System	Annual CO <sub>2</sub> Captured (10 <sup>6</sup> tonnes)
<b>United States</b>					
Baard Energy Clean Fuels (Wellsville, Ohio)	Coal+biomass to liquids	2013	53,000 barrels/day	Rectisol	N/A
DKRW Energy (Medicine Bow, Wyoming)	Coal to liquids	2014	20,000 barrels/day	Selexol	N/A
Summit Power (Penwell, Texas)	Coal IGCC	2014	400 MW <sub>g</sub>	Selexol	3.0
Taylorville Energy Center (Taylorville, Illinois)	Coal IGCC	2014	602 MW	N/A	N/A
Mississippi Power, Kemper County IGCC (Mississippi)	Lignite IGCC	2014	584 MW	N/A	N/A
Wallula IGCC (Walla Walla County, Washington)	Coal IGCC	2014	600-700 MW	N/A	N/A
Hydrogen Energy (Kern County, California)	Petcoke IGCC	2015	250 MW	N/A	N/A
Southern California Edison IGCC (Utah)	Coal IGCC	2017	500 MW	Selexol	3.5
FutureGen Alliance (Mattoon, Illinois) <sup>a</sup>	Coal IGCC	>2012 <sup>a</sup>	275 MW	N/A	N/A
<b>Outside the United States</b>					
GreenGen (Tianji Binhai, China)	Coal IGCC and poly-generation	2011 (stage I)	250 MW	N/A	N/A
Eston Grange IGCC (Teesside, UK)	Coal IGCC	2012	800 MW	N/A	5
Hartfield IGCC (Hartfield, UK)	Coal IGCC	2014	900 MW	Selexol	4.5
Genesee IGCC (Edmonton, Canada)	Coal IGCC	2015	270 MW	N/A	1.2
RWE Goldenbergwerk (Hurth, Germany)	Lignite IGCC	2015 <sup>b</sup>	360 MW	N/A	2.3

## Licensing Strategy

### Strategic Partners and Collaborators

### Oil and Gas Industry



Source: IHS Emerging Energy Research

Figure 4 - Positioning of Major Player in Carbon Capture Technology Supply [13]

### Membrane Industry

- Grace Membrane Systems (a division of W.R. Grace)
- Separex (now part of Honeywell's UOP)
- Cynara (now part of Natco)
- Medal (a division of Air Liquide)
- Membrane Technology and Research Inc.
- ABB Lummus Global (Randall Gas Technologies Division)

### Re-breather Industry

- The Underwater Systems Development and Acquisition Branch of Naval Surface Warfare Center Panama City Division (NSWC PCD), US Navy  
(<http://www.navsea.navy.mil/nswc/panamacity/BusOps/partnerships.aspx>)
- Extend Air (<http://www.extendair.com>)
- Kiss Re-breathers, Canada (<http://www.kissrebreathers.com>)

- Shearwater Research, Canada (<http://www.shearwaterresearch.com/company/>)
- Cochran Undersea Technology (<http://www.divecochran.com/computers/index.html>)
- Divex, U.K. (<http://www.divexglobal.com>)

### Next Steps

Current experiments at LBNL are focusing on chemical modification of the PANI surface, which leads to new chemistries optimized for CO<sub>2</sub> transport.

February 2013

## References

- [1] Blinova N., Stejskal J., Frechet J.M.J., Svec F., Effect of reaction conditions on film morphology of polyaniline composite membranes for gas separation. *J. Polym. Sci. A, Polym. Chem.* 50, 3077-3086, 2012.
- [2] Blinova N., Svec F., Polyaniline based membranes for separation of carbon dioxide and methane. *Prep. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 57 (1), 312-313, 2012.
- [3] Blinova N., Svec F., Functionalized polyaniline-based composite membranes with vastly improved performance for separation of carbon dioxide from methane. *J. Membr. Sci.* 423/424, 514-521, 2012.
- [4] Parker L., Folger P., Capturing CO<sub>2</sub> from Coal-Fired Power Plants: Challenges for a Comprehensive Strategy. University of Nebraska – Lincoln, 2010. Available at: <http://digitalcommons.unl.edu/cgi/viewcontent.cgi?article=1060&context=crsdocs>
- [5] NETL, DOE, Carbon capture technology research and Breakthrough Concepts. 2008. Available at: [http://www.netl.doe.gov/technologies/carbon\\_seq/refshelf/overviews/Carbon%20Capture%20Technology%20Research%20and%20Breakthrough%20Concepts.pdf](http://www.netl.doe.gov/technologies/carbon_seq/refshelf/overviews/Carbon%20Capture%20Technology%20Research%20and%20Breakthrough%20Concepts.pdf)
- [6] Baker R., Lokhandwala K., Natural Gas Processing with Membranes: An Overview. *Membrane Research and Technology*. 2007 Available at: <http://www.aseanenergy.info/abstract/31028885.pdf>
- [7] Freedonia, Membrane Separation Technologies to 2016 – Demand and Sales Forecasts, Market Share, Market Size, Market Leaders. Freedonia Group. 2012. Available at: <http://www.freedoniagroup.com/Membrane-Separation-Technologies.html>
- [8] Anderson C., Courtney E., Hamilton A., Mehta N., Reducing the Carbon Capture in Coal Plants. *Cleantech to Market*, Energy institute at Haas. 2011. Available at: <http://ei.haas.berkeley.edu/c2m/pdf/2011EndofYearSlides/Carbon%20Capture.pdf>
- [9] Folger P., Carbon Capture: An Assessment, Congressional Research Service. 2010. Available at: [http://www.cmu.edu/epp/iecm/rubin/PDF%20files/2010/CRS\\_Carbon%20Capture%20Tech%20Assessment\\_R41325\\_July%2019,%202010.pdf](http://www.cmu.edu/epp/iecm/rubin/PDF%20files/2010/CRS_Carbon%20Capture%20Tech%20Assessment_R41325_July%2019,%202010.pdf)
- [10] Brunetti A., Scura F., Barbieri G., Drioli E., Membrane Technologies for CO<sub>2</sub> separation, *J. Membr. Sci.* 359, 115-125, 2010.
- [11] Gopala K., Fabrication and Scale up of Polybenzimidazole (PBI) Membrane based system for precombustion based capture of carbon dioxide, NETL CO<sub>2</sub> Capture Technology Conference. 2010 Available at: <http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/thursday/Gopala%20Krishnan%20-%20NT%2043090.pdf>
- [12] Harned C., Navy uses life support expertise to improve miners' rebreather. *FLC Newslink*. 2012. Available at: <http://newslink.federallabs.org/2012/10/05/navy-uses-life-support-expertise-to-improve-miners-rebreather/>
- [13] IHS EER, Global Carbon Capture and Sequestration Markets and Strategies: 2010-2030. *Emerging Energy Research*. 2010. Available at: [http://www.emerging-energy.com/uploadDocs/Excerpt\\_GlobalCCSMarketsandStrategies2010.pdf.pdf](http://www.emerging-energy.com/uploadDocs/Excerpt_GlobalCCSMarketsandStrategies2010.pdf.pdf)